

## PATENT SPECIFICATION

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## (54) COMPLEXES OF BROMINE AND NONIONIC SURFACTANTS

(71) We, DIVERSEY LIMITED, a British Company of Cockfosters Road, Cockfosters, Barnet, Hertfordshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel complexes comprising bromine and ethylene oxide-containing nonionic surfactants with or without hydrochloric acid and possessing bactericidal properties against a wide range of micro-organisms. More particularly the invention relates to complexes of a similar type to those described in our copending Application No. 52517/68 (Serial No. 1,252,774).

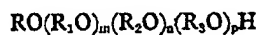
The halogens, chlorine, bromine and iodine are recognized as excellent bactericides and are used extensively, particularly in the food processing and handling industries, to prevent bacteriological contamination of foodstuffs. Halogen sanitizers are also used in controlling potentially harmful organisms in potable water, swimming pools, hospitals and almost anywhere that harmful organisms can present a contamination problem.

Chlorine, both as free chlorine and as the hypochlorite ion, bromine as free bromine and as the hypobromite ion, and iodine as free iodine or a solution of iodine in some co-solvent, have been widely used in sanitizing applications for many years. Iodine however suffers serious disadvantages in that iodine containing compositions can cause serious staining problems and if residual iodine comes into contact with foodstuffs, taste can be adversely affected.

Chlorine and bromine are extremely reactive chemically and are much more volatile than iodine. Heretofore, excessive loss of chlorine and bromine occurred especially in liquid compositions of high strength which

lost a substantial portion of their sanitizing effectiveness during storage. Moreover, highly concentrated solutions of chlorine or bromine have high vapour pressures causing the solutions to fume excessively, thus presenting a health hazard. When highly concentrated solutions of chlorine and bromine are diluted to use solutions, their fuming properties are still excessive. Furthermore, chlorine and bromine are highly corrosive materials and cannot be used to sanitize many materials because of their corrosive properties. Also, chlorine and bromine in many compositions now available are irritating to human tissue.

The present invention provides a complex of bromine and any nonionic surfactant of the formula:



where R is hydrogen, an alkyl group, or a fatty acid acyl group,  $R_1$  and  $R_3$  which may be the same or different are either ethylene or a mixture of ethylene and alkenes having from 3 to 8 carbon atoms and the oxygen/carbon ratio in the  $(R_1O)_m$  and  $(R_3O)_p$  hydrophilic groups exceeds 0.4,  $R_2$  is any alkylene group having from 2 to 8 carbon atoms or a mixture thereof, m is any number from 1 to 150, n is any number from 0 to 150 and p is any number from 0 to 150, the sum of m, n and p being at least 3.

Some classes of nonionic surfactants which can be used to complex bromine and form complexes within the scope of this invention are:

1. Polyalkyleneoxy alcohols
2. Polyalkylene oxide block copolymers
3. Polyalkyleneoxy esters of fatty acids

The polyalkyleneoxy alcohols useful in producing these complexes can be represented by the formula:



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where R is any alkyl or fatty acid acyl group,  $R_1$ ,  $R_2$ , m and p have the meanings defined above and the sum of m and p is at least 3.

5 Polyethyleneoxy alcohol surfactants of the formula:



where R is any alkyl group having from 11 to 15 carbon atoms and m is a number from 3 to 30 are particularly useful in making bromophors.

10 The polyalkylene oxide block copolymers useful in producing these complexes can be represented by the formula:



15 where R is hydrogen or an alkyl group preferably having 1 to 8 carbon atoms and  $R_2$  is any alkylene group having from 2 to 8 carbon atoms or mixtures thereof and the oxygen/carbon ratio in the  $(R_2O)_n$  hydrophobic group does not exceed 0.4,  $R_1$  is any alkylene group having from 2 to 8 carbon atoms or mixtures thereof and the oxygen/carbon ratio in the  $(R_1O)_m$  hydrophilic group exceeds 0.4, n represents any number from 1 to 70, and m represents any number from 2 to 150.

25 The polypropyleneoxy polyethyleneoxy ethanol block polymers useful in producing these complexes can be represented by the formula:

30  $HO(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_cH$  where b represents any number from 10 to 70 and a and c represent any numbers from 2 to 150.

35 The alkyl mixed polypropyleneoxypolyethyleneoxy polyethyleneoxy ethanol heteric-block polymers useful in producing these complexes can be represented by the formula:



40 where R is any alkyl group having from 1 to 8 carbon atoms, a is any number from 14 to 49, b is any number from 1 to 10, and the weight ratio of a to b is within the range of 95:5 to 85:15, and c is any number from 18 to 100.

45 Butoxy mixed polypropyleneoxypolyethyleneoxy polyethyleneoxy ethanol heteric-block polymer surfactants of the formula:



50 where a is 21, b is 3 or 4, and c is any number from 27 to 48 are specially useful in making bromophors.

The polyethyleneoxy esters of fatty acids useful in producing these complexes can be represented by the formula:

55  $RCOO(R_1O)_mH$

where R is any alkyl group having from 7 to 23 carbon atoms,  $R_1$  is either ethylene or a mixture of ethylene and alkynes having from 3 to 8 carbon atoms and the oxygen/carbon ratio in the  $(R_1O)_m$  hydrophilic group exceeds 0.4, and m is any number from 3 to 40.

60 Polyethyleneoxy esters of fatty acids of the formula:



where R is an alkyl group having from 10 to 18 carbon atoms and m is any number from 5 to 40, are particularly useful surfactants for making bromophors.

The complexes provided by this invention can be readily produced by combining the non-ionic surfactant and bromine under suitable reaction, or complexing conditions. It is generally advisable to use liquid bromine and to combine it with the surfactant in liquid form. Many of the surfactants are liquid at ambient temperature but those that are not can be heated to liquefy them. Reaction between the liquid bromine and liquid surfactant is generally highly exothermic. Therefore, the reaction mixture should be stirred vigorously, and cooled if necessary, as the bromine is added slowly to the liquid surfactant. It is generally advisable to maintain the temperature of the reaction mixture at 20°F. to 200°F. for satisfactory results. When it is desired to increase the temperature of the reaction mixture, the rate of addition of the bromine can be increased. Following addition of the bromine the reaction mixture can be stirred to facilitate complete reaction. The reaction mixture can then be cooled to ambient temperature. The resulting composition comprising a bromophor of bromine and a nonionic surfactant can be packaged and stored. Complexes which are solid at ambient temperature can be prilled or granulated to improve subsequent handling and use. However, most bromophors produced from solid surfactants are liquids at ambient conditions and can be used in such form.

The amount of bromine complexed with the nonionic surfactant can be varied through rather wide limits. Thus, on a weight basis, 1 part of bromine can be complexed with from 1 to 9 parts of surfactant. Although as little as 10% bromine can be used, it is generally not practical to combine less than 1 part bromine with 4 parts of surfactant. Furthermore, usually not more than about 1 part of bromine is complexed with 1 part of surfactant since higher amounts of bromine may not give complexes with the desired stability.

In addition, the amount of bromine which can be complexed will vary to some extent with the various nonionic surfactants used. The most suitable complexes obtained however are those formed by complexing 1 part by weight of bromine with 1.5 to 3 parts of surfactant.

115 It has furthermore been found that the

lengths of the polyethyleneoxy chain in the surfactant has a direct effect on the amount of bromine which can be complexed, the availability of the complexed bromine and the stability of the complex during storage. Generally, as the length of the polyethyleneoxy chain increases, so does the amount of available bromine in the resulting complex. However, after a certain length of polyethyleneoxy group is reached the stability of the resulting complex decreases as shown by storage tests with loss of available bromine even though more available bromine may be initially present as the length of the polyethyleneoxy group increases above this point. The subsequent working examples will further illustrate this and show the advisability of correlating the polyethyleneoxy chain length with desired maximum storage stability.

Another novel finding of this invention is that even more stable complexes can be obtained by having a small amount of hydrochloric acid present in the reaction mixture during formation of the bromine-nonionic surfactant complex. Advisably, the hydro-

chloric acid is combined with the surfactant before the surfactant and bromine are combined. Concentrated hydrochloric acid is advisably used since added water is unnecessary. However, dilute hydrochloric acid can also be used. Nevertheless, water is not considered beneficial since too much water can cause phase separation during preparation of the complex and subsequent storage or dilutions. The amount of hydrochloric acid is not critical. Generally, 1 part by weight of concentrated hydrochloric acid (37%) to 3 to 100 parts of surfactant can be used.

The next section of this disclosure is divided into several parts, each part disclosing complexes belonging to each class of nonionic surfactant disclosed heretofore.

#### Part 1

##### Polyethyleneoxy Alcohols

The first group of alkyl polyethyleneoxy ethanols to be considered are linear primary alcohol polyethyleneoxy ethanols. This group can be represented by the formula



where  $m$  is any number from 9 to 13 and  $n$  is any number from 3 to 30.

Four different linear alcohol mixtures are disclosed herein. However, disclosure of these alcohol mixtures is understood to be for purposes of example only. This invention is not limited to use of these four alcohol complexes within the group of linear primary alcohol polyethyleneoxy ethanols.

##### Example 1.

A series of bromophors was produced by reacting various linear primary alcohol polyethyleneoxy ethanol surfactants, having different mole ratios of ethylene oxide, with liquid bromine. A ratio of 63.3 parts by weight of surfactant to 36.7 parts by weight of bromine was reacted. The procedure used to produce these bromophors follows and is illustrated by the specific use of a linear primary alcohol polyethyleneoxy ethanol wherein the linear alcohol group is composed of a mixture of linear alcohols with the following amounts of carbon atoms in each linear alcohol, to wit,  $\text{C}_{12}$ —20%,  $\text{C}_{13}$ —30%,  $\text{C}_{14}$ —30%,  $\text{C}_{15}$ —20%, and which mixture of linear primary alcohols is ethoxylated with 9 moles of ethylene oxide.

100 grams of the above described surfactant was placed in a 400 ml beaker. This beaker of surfactant was placed on a magnetic stirring

apparatus. A 1 1/2 inch stirring bar was used. A thermometer was suspended in the surfactant and the surfactant was stirred as vigorously as possible without stirring air into the surfactant. 58 grams of bromine was added to the surfactant slowly. The 58 grams of bromine was added from a 50 ml burette. The 58 grams of bromine at 25°C. is approximately equivalent to 18.7 ml of bromine. The temperature of the reaction mixture was allowed to rise slowly to 140°F. and when the temperature reached that point, the addition of the bromine was stopped. The reaction mixture was allowed to cool to 120—130°F. and then the addition of bromine to the reaction mixture was recommenced. Addition of the bromine was continued until the temperature of the reaction mixture again reached 140°F. The reaction mixture was allowed to cool as before to 120—130°F. This cycle of additions and coolings was continued until all 58 grams of bromine was combined with the surfactant. The reaction mixture was then allowed to cool to ambient temperature. A red-brown bromophor premix was obtained with an initial available bromine of 25.1% by weight.

Table 1 following lists the various surfactants used in making bromophors according to this procedure and gives pertinent physical and stability data pertaining to them.

Hyd Com	be m*	ant Me o Ethy. Oxide	ility of	r Primu	ohol P	leneos	mol Br	ors at	°F.
			Av Br Effic	%	utial	Wk.	it by V ; Wks.	of Ava 4 Wks.	3ronin 8 Wks.
		7.5			4.0	20.7	19.2	17.4	15.3
		6.5			4.2	21.0	18.7	16.8	14.7
		3			4.8	21.4	19.2	18.1	15.4
		7			4.7	19.4	16.9	15.7	13.2
		9			5.1	20.1	18.0	16.9	14.2
		12			3.3	18.9	16.5	14.4	12.2
		30			3.1	17.9	16.0	15.2	12.2
* Hyd Com	obe C tion B re of	tion A ses the rimary	ises ti ing mi cohol	wing i f linear f—20%	of lin ry fatty —30%	inary als: C <sub>1</sub> 30%, C <sub>2</sub> 30%	cohol s: C <sub>13</sub> 30%	—33.3% Hydr	—33.3 Com
		1.	minat	Table	ses:	adde	ny sur	dislo	Table
		5	t in a	d diff	ts wid	befor	romine	mine, th	nount
		5	droph	uracra	amount	avail	e incr	the av	broni
		5	oxide,	es the	le with	stabi		Exami	illustra
		5	amoph	more	s mol	this.			
		5	that α	that su	it show				
		5	oxide	lity.					
		5	romin	moles	ylene	Br	ors wi	le 2.	ombini
		5	he nun	ies of	2.3 )	chlor	y wei	pared	d hyd.
		5	in ti	of	chlor	of 1	h 61 f	h 61 f	y wei
		5	bove, t	ilable	ie eff	prima	etol	etol	ylene
		5	up to	it and	leas	ethar	rfracta	vario	dropic
		5	t foun	if hy	xric ac	comf	is and	us mo	ethyl



Hydrocarbon	Structure	Formula	Boiling Point (°C)	Density (g/cm³)	Refractive Index (D <sub>20</sub> <sup>20</sup> )	Viscosity (cP)	Flash Point (°C)	Freezing Point (°C)	Other Properties
Hydrocarbon 1	Structure 1	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid
Hydrocarbon 2	Structure 2	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid
Hydrocarbon 3	Structure 3	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid
Hydrocarbon 4	Structure 4	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid
Hydrocarbon 5	Structure 5	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid
Hydrocarbon 6	Structure 6	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid
Hydrocarbon 7	Structure 7	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid
Hydrocarbon 8	Structure 8	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid
Hydrocarbon 9	Structure 9	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid
Hydrocarbon 10	Structure 10	C <sub>10</sub> H <sub>18</sub>	100	0.71	1.45	1.0	10	-10	Clear, colorless liquid

TAB (contir

Hy C s	St be M E	% nt fo e bi	HCl In unt o tion	ble ne ncy	initial	1 Wk.	recent b 2 Wks.	ght of l 4 Wks.	de Broi 8 Wk	16 Wk	24 W
				2	22.1	18.4	17.5	15.1	13.4	11.1	9.
				3	22.2	19.6	18.6	15.4	14.4	11.1	10.
				2	24.2	20.1	18.5	17.0	14.4	12.1	10.
				6	23.7	21.1	20.9	19.0	17.4	17.1	15.
				7	27.4	23.5	23.4	21.7	19.4	19.1	17.
			e	0	23.5	20.9	19.4	17.1	14.4	11.1	11.
			i	6	24.8	21.0	19.5	17.6	15.4	12.1	10.
			i	3	24.7	20.9	19.7	17.9	15.1	12.1	10.
			i	9	23.1	20.4	19.5	18.1	15.1	13.1	13.
			i	1	23.9	19.9	18.7	17.1	15.1	13.1	11
			e	9	24.2	21.0	18.7	16.8	14.1	12.1	11
			i	4	25.1	20.8	18.7	16.8	13.1	11.1	9
			)	4	25.1	20.7	19.6	17.4	14.1	11.1	10
			)	1	27.2	23.3	22.5	21.8	20.1	17.1	15
			)	5	28.8	25.0	23.9	21.4	20.1	16.1	15

TABLE (contin

Hyd. Con- sit	Sur- face Mo- Bic- C	t o Su- bro	ICI it on	le e y	initial	Wk.	ent by Wks.	ut of A <sup>1</sup> Wks.	Brom 8 Wks.	16 Wks.	24 Wks.
					1.2	9.9	18.7	17.3	14.9	13.2	12.6
					1.8	9.3	18.8	15.8	12.7	11.7	10.8
					1.7	0.0	17.7	16.2	13.9	12.0	11.5
					1.9	1.9	20.7	19.1	18.3	17.6	16.2
					1.2	2.4	20.3	19.8	18.9	18.0	17.1
					1.7	9.4	16.9	15.7	13.2	11.1	10.0
					1.3	10.3	18.5	16.1	14.0	11.2	9.7
					1.6	11.6	19.1	17.2	14.1	11.6	10.0
					3.0	12.9	21.4	20.0	19.2	17.0	14.4
					3.9	13.9	22.9	20.9	20.1	18.1	15.1
					5.1	10.1	18.0	16.9	14.3	11.4	11.1
					2.5	9.9	18.2	16.3	14.7	11.8	11.3
					4.0	11.2	20.0	17.4	15.6	13.0	11.5
					5.1	12.6	22.2	21.1	20.2	17.1	16.4
					3.0	13.8	23.2	21.8	20.4	18.5	16.1

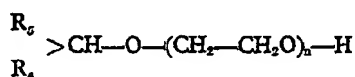


H <sub>2</sub> O	to be used	ant ratio ne e t	HCl in tant to ation	lab line ency o	TA	i (cont	percent 2 Wt	light of 4 Wt	ble Br 8 W	16 W	24 W
					Initial	1 Wt.					
			ne	.5	23.3	18.9	16.5	14.	12.	10	9
			5	.1	22.8	18.8	18.3	16.	13.	10	9
			0	.9	23.1	20.1	18.6	16.	14.	12	10
			0	.9	26.4	22.3	22.1	20.	19.	18	15
			0	.7	28.5	24.7	23.5	21.	21	19	17
			ne	.9	23.1	17.9	16.0	15.	12	10	8
			5	.8	21.2	16.9	15.7	14.	12	10	9
			0	.9	22.7	18.9	17.1	14.	12	10	9
			0	.8	26.0	21.8	20.8	19.	18	16	14
			0	.6	28.1	24.0	20.0	19.	19	18	17

\* {  
note }

The data in Table 3 shows that the more hydrochloric acid in the surfactant, the greater is the available bromine efficiency of the bromophor. It is also to be noted that the actual amount of available bromine increases as the amount of hydrochloric acid increases.

The second group of alkyl polyethyleneoxy ethanols to be considered are secondary alcohol polyethyleneoxy ethanols. This group can be represented by the formula



where  $R_c$  and  $R_a$  are alkyl groups and

$R_c-CH-R_a$  has 10 to 18 carbon atoms and  $n$  is any number from 3 to 30. As with the linear primary alcohol polyethyleneoxy ethanols, the examples cited below are not to be construed to be limiting for the purposes of this disclosure.

#### Example 4.

A series of bromophores was produced by reacting various linear secondary alcohol polyethyleneoxy ethanol surfactants with and without hydrochloric acid (37%), having different

mole ratios of ethylene oxide with liquid bromine. A ratio of 63.3 parts by weight of surfactant, or a surfactant-hydrochloric acid (37%) mixture, to 36.7 parts by weight of bromine was reacted. This example is illustrated by the specific use of a linear secondary alcohol polyethyleneoxy ethanol of a hydrophobe chain length mixture of from 11 to 15 carbon atoms and containing 12 moles of ethylene oxide in each surfactant molecule. Either the straight surfactant or a surfactant-hydrochloric acid mix was used. If a surfactant-hydrochloric acid mixture was used, 0.5, 1.0, 5.0 and 10.0% hydrochloric acid (37%) was placed in the surfactant. In the procedure, 95 grams of surfactant was placed in a 400 ml. beaker and 5 grams of concentrated hydrochloric acid (37%) was added to the surfactant and mixed thoroughly with the surfactant. The resulting 100 grams of surfactant-hydrochloric acid (37%) mix was then brominated with 58 grams of bromine as described in Example 1. A red-brown bromophor was obtained which contained 18.9% available bromine initially. Table 4 describes the other bromophors made according to this example. It is to be noted that 100 grams of straight surfactant or surfactant-hydrochloric acid (37%) mix was used throughout.

TABLE 4

Stability at 75—80°F. of Linear Secondary Alcohol Polyethyleneoxy  
Ethanol-Hydrochloric Acid Bromophors With Varying Amounts of Hydrochloric Acid

3	None	49.3	18.1	9.0	not tested — beyond 1 week
3	0.5	47.9	17.6	8.3	
3	1.0	47.4	17.4	8.0	
3	5.0	46.3	17.0	9.3	
3	10.0	49.0	18.0	7.7	
7	None	45.2	16.6	10.6	not tested beyond 1 week
7	0.5	49.0	18.0	9.3	
7	1.0	50.1	18.4	11.6	
7	5.0	50.4	18.5	10.0	
7	10.0	52.9	19.4	12.0	
9	None	46.0	16.9	11.5	not tested beyond 1 week

TABLE A (continued)

Surfactant Mole Ratio of Ethylene Oxide	% Conc HCl (37%) in the Surfactant prior to Bromination	Available Bromine Efficiency %	Percent by Weight of Available Bromine		
			Initial	1 Wk.	4 Wks.
9	0.5	45.5	16.7	11.1	
9	1.0	49.9	18.3	11.2	
9	5.0	50.4	18.5	13.5	
9	10.0	57.2	21.0	12.4	
12	None	43.3	15.9	9.8	9.3
12	0.5	45.2	16.6	11.7	9.1
12	1.0	46.0	16.9	12.6	9.4
12	5.0	51.5	18.9	14.2	9.3
12	10.0	56.7	20.8	13.8	1.2

This group of surfactants gives generally less acceptable results when made into a bromophor than other nonionic surfactants.

2 to 150. Examples of this class of surfactants made into bromophors follows.

#### Example 5.

78.6 grams of a polypropyleneoxy polyethyleneoxy ethanol with 28 moles of propylene oxide in the central hydrophobe and 10 moles of ethylene oxide in each of the two side hydrophilic groups was placed in 200 ml beaker. To this quantity of surfactant, 3.6 grams of concentrated hydrochloric acid (37%) was added. This surfactant-hydrochloric acid mix was then brominated with 17.8 grams of bromine at a temperature of 120°F. as described in Example 1. A clear, red-brown liquid was obtained which had an initial available bromine of 12.7%. Table 5 gives the stability data for this example.

5

#### Part 2

#### Polyalkylene Oxide Block Copolymers

The first group within this part of the disclosure concerns polypropyleneoxy polyethyleneoxy ethanol-bromine complexes. This group of surfactants can be represented by the formula:



where b represents any number from 10 to 70, and a and c represent any number from

TABLE 5

Stability of the Bromophor of Example 5

Time	% Available Bromine	
	Room Temperature	100°F.
Available bromine efficiency, %	71.3	71.3
Initial	12.7	12.7
7 Months	6.96	1.63
2 years	4.12	—

Surfactant Used	Conc. %	Temp. °F.	Time	Remarks	Notes	Ref.
5	10	100	10	10	10	10
10	10	100	10	10	10	10
15	10	100	10	10	10	10
20	10	100	10	10	10	10
25	10	100	10	10	10	10
30	10	100	10	10	10	10
35	10	100	10	10	10	10
40	10	100	10	10	10	10
45	10	100	10	10	10	10
50	10	100	10	10	10	10
55	10	100	10	10	10	10
60	10	100	10	10	10	10
65	10	100	10	10	10	10
70	10	100	10	10	10	10
75	10	100	10	10	10	10
80	10	100	10	10	10	10
85	10	100	10	10	10	10
90	10	100	10	10	10	10
95	10	100	10	10	10	10
100	10	100	10	10	10	10

Since different analytical methods for determining bromine content may give different results, the procedure actually used in determining the available bromine content of the bromophors of the various examples will be given for making reproducible comparisons. The procedure was as follows:

500 to 800 ml of distilled water is placed in a 1000—2000 ml beaker. The water is stirred vigorously with a stirring apparatus, such as a magnetic stirrer or a paddle stirrer, with care not to stir air into the water.

A weighed sample of a bromophor is transferred as quickly as possible with a wash bottle into the stirred water. The final result will be adversely affected if the sample is not dissolved as quickly as possible. If the sample is slowly soluble in water such as would occur in a viscous bromophor, the sample is predissolved in reagent grade t-butanol. Then the t-butanol solution of the bromophor is poured into the stirred water and rinsed in with a wash bottle as quickly as possible.

To the mixture is quickly added 10 ml of 40% w/v potassium iodide followed by quick addition of 10 ml of glacial acetic acid. Enough 30% Triton (Trade Mark) X—102 solution is added to clarify the sample solution. The solution is then titrated with 0.1 sodium thiosulphate to a colourless endpoint. The bromine is then calculated from the resulting data.

The bromophors produced as described, as well as others within the scope of this invention, can be added to water to produce a useful solution or dispersion containing any desired practical concentration of available bromine. When applied to surfaces the solution or dispersion gradually releases bromine which is effective in combating microorganisms. Use solutions containing 0.1 to 500 ppm of bromine are particularly useful antibacteriologically.

It has been further discovered that when a bromophor is dissolved in water to make a use solution, it is stabilized by the presence of hard water salts which may exert a buffering action on the solution. If a small amount of alkaline buffering material is present in the water, the bromophor solution is buffered up to a near neutral pH. Any water with sufficient temporary hardness or bicarbonate hardness, should exhibit this buffering property. Some of the other buffering agents which can be used are tetrasodium pyrophosphate and sodium tripolyphosphate.

Thus, bromophors are more bactericidally effective dissolved in water containing temporary hardness than they are when they are dissolved in water containing no temporary hardness. This is true because the bromine is more stable in water with temporary hardness than water without temporary hardness or any other buffering or alkalizing agent present.

The solutions thus produced may be employed to combat microorganisms domestically

and industrially. For example, such solutions may be applied to paper in the course of its manufacture to control mould and fungi. They may be used for cleaning surfaces to ensure sanitary conditions, such as for the cleaning of floors, walls, sinks, bowls, tanks, pasteurizers and pipelines, as a rinse for dishes and kitchen utensils, and as a germicidal composition.

WHAT WE CLAIM IS:—

1. A complex of bromine and any nonionic surfactant of the formula:



where R is hydrogen, an alkyl group, or a fatty acid acyl group,  $R_1$  and  $R_3$  which may be the same or different are either ethylene or a mixture of ethylene and alkylenes having from 3 to 8 carbon atoms and the oxygen/carbon ratio in the  $(R_1O)_m$  and  $(R_3O)_n$  hydrophilic groups exceeds 0.4,  $R_2$  is any alkylene group having from 2 to 8 carbon atoms or a mixture thereof, m is any number from 1 to 150, n is any number from 0 to 150, and p is any number from 0 to 150, the sum of m, n and p being at least 3.

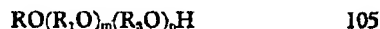
2. A complex as claimed in claim 1 containing 1 part by weight of bromine and 1 to 9 parts by weight of surfactant.

3. A complex as claimed in claim 2 containing 1 part by weight of bromine and 1.5 to 4 parts by weight of surfactant.

4. A complex as claimed in any of claims 1 to 3 in admixture with hydrochloric acid.

5. A complex as claimed in claim 4 in admixture with 1 part by weight of hydrochloric acid (37%) with 3 to 100 parts by weight of surfactant.

6. A complex as claimed in any of claims 1 to 5 in which the surfactant is any polyalkyleneoxy alcohol of the formula:



where R is any alkyl or fatty acid acyl group,  $R_1$ ,  $R_3$ , m and p have the meanings defined in claim 1 and the sum of m and p is at least 3.

7. A complex according to claim 6 in which the surfactant is a polyethyleneoxy alcohol of the formula:



where R is any alkyl group having from 11 to 15 carbon atoms and m is a number from 3 to 30.

8. A complex as claimed in claim 6 in which the surfactant is any linear alcohol polyethyleneoxy ethanol.

9. A complex as claimed in claim 6 in which the surfactant is any secondary alcohol polyethyleneoxy ethanol.

10. A complex as claimed in any of claims 1 to 5 where the surfactant is a polyalkylene oxide block copolymer of the formula:



oxy ester of a fatty acid of the formula:

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- where R is hydrogen or an alkyl group having 1 to 8 carbon atoms,  $\text{R}_1$  is an alkylene group having from 2 to 8 carbon atoms or mixtures thereof and the oxygen/carbon ratio in the  $(\text{R}_2\text{O})_n$  group does not exceed 0.4,  $\text{R}_1$  is an alkylene group having from 2 to 8 carbon atoms or mixtures thereof and the oxygen/carbon ratio in the  $(\text{R}_1\text{O})_m$  group exceeds 0.4, n represents any number from 1 to 70 and m represents any number from 2 to 150.

11. A complex as claimed in claim 10 in which the surfactant is a polypropyleneoxy polyethyleneoxy ethanol block polymer of the formula:



where b represents any number from 10 to 70 and a and c represent any number from 2 to 150.

12. A complex according to claim 11 where the surfactant is a polypropyleneoxy polyethyleneoxy ethanol block polymer of the formula:



13. A complex as claimed in claim 10 in which the surfactant is any alkyl mixed polypropyleneoxypolyethyleneoxy polyethyleneoxy ethanol heteric-block polymer of the formula:



- where R is any alkyl group having from 1 to 8 carbon atoms; a is any number from 14 to 49 and b is any number from 1 to 10 and the weight ratio of a to b lies within the range of 95:5 to 85:15; and c is any number from 18 to 100.

14. A complex according to claim 13 in which the surfactant is a butoxy mixed polypropyleneoxypolyethyleneoxy polyethyleneoxy ethanol heteric-block polymer of the formula:



where a is 21, b is 3 or 4, and c is any number from 27 to 48.

15. A complex as claimed in any of claims 1 to 5 where the surfactant is a polyethylene-

where R is any alkyl group having from 7 to 23 carbon atoms,  $\text{R}_1$  is either ethylene or a mixture of ethylene and alkenes having from 3 to 8 carbon atoms and the oxygen/carbon ratio in the  $(\text{R}_1\text{O})_m$  group exceeds 0.4, and m is any number from 3 to 40.

16. A complex according to claim 15 in which the surfactant is a polyethyleneoxy ester of a fatty acid of the formula:



where R is an alkyl group having from 10 to 18 carbon atoms and m is any number from 5 to 40.

17. A complex as claimed in any of claims 1 to 16 substantially as herein described with reference to the Examples.

18. The method of producing a bromophor as claimed in claim 1 which comprises combining bromine and a nonionic surfactant as defined therein at a temperature of from 10°C to 95°C and then cooling the resulting complex to ambient temperature.

19. A method as claimed in claim 18 in which the mixture contains 1 part by weight of bromine and 1 to 9 parts by weight of surfactant.

20. A method as claimed in claim 18 or claim 19 in which the surfactant is combined with hydrochloric acid before being combined with the bromine.

21. A method as claimed in claim 18 substantially as herein described with reference to the Examples.

22. A use solution comprising a complex as claimed in any of claims 1 to 17 in an aqueous medium.

23. A use solution as claimed in claim 22 in which the use solution contains from 0.1 to 500 ppm bromine.

24. A use solution as claimed in claim 22 substantially as herein described.

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